Diffusion-reaction in thermal growth of silicon oxide films on Si

R.M.C. de Almeida*, S.Gonçalves*, I.J.R. Baumvol*, and F.C. Stedile**

*Instituto de Física and **Instituto de Química
Universidade Federal do Rio Grande do Sul
Av. Bento Gonçalves 9500, Porto Alegre, RS 91509-900
Brazil

The thermal growth of silicon oxide films on Si in dry O_2 is modelled as a dynamical system, assuming that it is basically a diffusion-reaction phenomenon. Relevant findings of the last decade are incorporated, as structure and composition of the oxide/Si interface and O_2 transport and reaction at initial stages of growth. The present model departs from the well established Deal and Grove framework (Deal, B.E. and Grove, A. S. General Relationship for the Thermal Oxidation of Silicon *J. Appl. Phys.* **36**, 3770-3778 (1965)) indicating that its basic assumptions, steady-state regime and reaction between O_2 and Si at a sharp oxide/Si interface are only attained asymptotically. Experimental growth kinetics by various authors, obtained for a wide range of growth parameters are shown to collapse into one single curve when the scaling properties of this model equations are explored.

Silicon oxide films thermally grown on single-crystalline Si (c-Si) wafers in dry O_2 are still the most common materials used as gate dielectrics in Si-based metal-oxide-semiconductor (MOS) structures. As device dimensions shrink below 0.25 μm, the oxide films are forced to scale down to thicknesses of 5 nm and less. Reliability of highly integrated Si devices is critically dependent on the characteristics of the vitreous oxide film, like thickness uniformity, defect density, dielectric strength, and others, as well as on those of the oxide/Si interface, like roughness, electronic states density and others [1,2].

The dielectric performance of ultrathin films of silicon oxide thermally grown on Si and the structural and electronic properties of the oxide/Si interface have been intensively studied experimentally, theoretically, and computationally [3,4] in synergism with the development of the semiconductor industry. The understanding of film growth kinetics, however, did not make any significant progress since the early model of Deal and Grove [5], which subsisted as the only fundamental approach. The Deal and Grove model, and more specifically the resulting linear-parabolic law, agrees with the observed growth kinetics in dry O_2 only above a certain thickness [6–8]. This is an expected fact from the model itself, since its basic assumption is that growth is promoted by interstitial diffusion of the oxidant species, the O_2 molecule, through a previously grown oxide layer, thick enough to guarantee steady state regime. Besides, reaction between O_2 and Si is assumed to take place solely at an abrupt oxide/Si interface, producing stoichiometric SiO_2. This initial oxide thickness was estimated [6,5] from experimental data as being between 20 and 30 nm, well above the thickness range of interest for present and future use in microelectronics Si-devices. Description of the growth kinetics in the lower thickness range was addressed by many authors, within the Deal and Grove model framework, adding new terms to the linear-parabolic expression in order to fit experimental data [6,7]. Although fitting the experimental curves, and so providing useful

analytical expressions capable of reproducing the whole thickness interval, the extra terms added to the Deal and Grove expression did not have a well-defined physical meaning, even though their dependence on some processing parameters, like temperature for instance, could be explored [6]. None of these models has been shown to be clearly correct and none of them has gained widespread acceptance. One is left then with several empirical expressions which can be used to model the growth kinetics in dry O_2 in the thin and ultrathin film regimes below 20 nm, as well as in further stages of growth, but with no satisfactory physical explanation [9]. According to B. Deal [10] "such an expression may well fit the data, but provides little guidance or insight into mechanisms involved or effects of process variations".

Recent investigations showed that as film thickness decreases below 20 nm, the contribution to film growth due to reaction away from the interface region becomes increasingly significant [11–16]. Furthermore, there are strong theoretical and experimental evidences of the existence of a reactive layer formed by sub-oxides (also called Si-excess) near the oxide/Si interface [17–20].

In the present work the thermal growth of silicon oxide films on Si is modelled as a dynamical system, assuming that it is basically a diffusion-reaction phenomenon. Since steady-state regime is not imposed, an initial oxide thickness is not required. Therefore, the model is expected to describe the whole oxide thickness interval. Diffusion-reaction equations have been used to describe different systems [21–23] but, to our knowledge, this is the first time they are applied to silicon oxide growth kinetics. The diffusing species is taken to be O_2, to model what has been largely demonstrated by isotopic substitution experiments [11,12,24–26]. Growth is promoted by reaction of O_2 with Si, not necessarily at the oxide/Si interface, but wherever the two species meet. The growth kinetics can then be obtained at any temperature by specifying the diffusivity of the O_2 molecule in the silica network, D, the reaction rate between O_2 and

Si, k, and the O_2 pressure in the gas phase. Growth in one dimension is considered, which is the most common experimental situation, meaning that as a face of c-Si is exposed to O_2, the silica film grows in the direction perpendicular to this face. The proposed description for the growth kinetics is contained in the following coupled partial differential equations:

$$\frac{\partial \rho_{O_2}}{\partial t} = D\frac{\partial^2 \rho_{O_2}}{\partial x^2} - k\rho_{O_2}\rho_{Si}$$
$$\frac{\partial \rho_{Si}}{\partial t} = -k\rho_{O_2}\rho_{Si} \tag{1}$$

where $\rho_i = c_i/c_{Si}^{bulk}$ is the concentration of the i-species ($i = Si$, O_2) in the solid phase, in units of number of atoms per unit volume, c_i, normalised by the concentration of Si in c-Si, c_{Si}^{bulk}. Thus, the state of any species at any time is characterised by a density function $\rho(x,t)$, where x is the coordinate in the direction of growth, $x = 0$ indicating the surface of the sample, and t is the elapsed growth time. The first equation describes the O_2 concentration rate and it is essentially a balance equation. At a given position the concentration of oxygen may vary due to the net flux of O_2 through fully (SiO_2 in oxide bulk) or partially (SiO_x, $x < 2$, near the interface [4,16,19,20]) oxidised Si, modelled by the diffusion term with a diffusion constant D, or due to reaction to produce silicon oxide, characterised by a reaction rate constant k. The second equation describes the Si concentration rate, which is only due to reaction with O_2, implying that Si is an immobile species [24]. The silicon oxide concentration, ρ_{oxide}, does not explicitly appear in these equations, but it is in direct connection with ρ_{Si} through the expression

$$\rho_{oxide}(x,t) = 1 - \rho_{Si}(x,t) \tag{2}$$

reflecting conservation of Si species in the Si + O_2 → SiO_2 reaction. It is assumed that the O_2 diffusivity at a certain temperature does not change during oxidation, and therefore D is constant throughout the whole growth process. Furthermore, based on the fact that oxygen diffuses mainly through oxide, one neglects volume changes due to the above chemical reaction. In order to complete the description in terms of equations (1), it is necessary to provide the initial and boundary conditions. They are

$$\rho_{Si}(x,0) = 1 \quad \forall x \geq 0 \tag{3}$$
$$\rho_{O_2}(0,t) = \frac{c_{gas}f_v}{c_{Si}^{bulk}} \quad \forall t \geq 0$$

where c_{gas} is the O_2 concentration in the gas phase and f_v is the ratio between the accessible free volume for O_2 in the silica network and the unit volume of the solid [8]. Initially there is a pure, c-Si substrate from $x = 0$ to ∞, whose surface is exposed to a gaseous medium, O_2, with a relative concentration at this surface represented in the second condition by $\frac{c_{gas}f_v}{c_{Si}^{bulk}}$. Reaction of these two species produces silicon oxide, not necessarily stoichiometric, as

the solid-phase reaction Si + O_2 → SiO_2 may occur in several steps. As time proceeds, O_2 diffuses through the oxide network, reaches Si, reacts producing more oxide, and consequently pushes the oxide/Si interface further in the positive x region. Different values of D, k and c_{gas} imply different kinetics. However, the values of D and k may be used to define "natural" units for the system, resulting in a set of adimensional equations with only one parameter, namely c_{gas} [23]. Under the following transformations:

$$\tau = tk$$
$$u = x\sqrt{\frac{k}{D}} \tag{4}$$
$$\phi_i(u,\tau) = \rho_i(x,t) \quad \text{for } i = Si, O_2, oxide$$

the resulting adimensional set of differential equations and initial and boundary conditions are

$$\frac{\partial \phi_{O_2}}{\partial \tau} = \frac{\partial^2 \phi_{O_2}}{\partial u^2} - \phi_{O_2}\phi_{Si}$$
$$\frac{\partial \phi_{Si}}{\partial \tau} = -\phi_{O_2}\phi_{Si} \tag{5}$$
$$\phi_{Si}(u,0) = 1 \quad \forall u \geq 0$$
$$\phi_{O_2}(0,\tau) = \frac{c_{gas}f_v}{c_{Si}^{bulk}} \quad \forall \tau \geq 0$$

leaving c_{gas} as the only parameter. This is a powerful statement. It predicts that in all experiments performed at the same gas pressure, oxide growth kinetics and O_2 and Si concentrations versus depth curves (profiles) at different temperatures collapse to the same curves, provided that appropriate units are used: $1/k$ for time and $\sqrt{D/k}$ for thickness.

In order to obtain profiles and growth kinetics, eqs.(5) must be solved. Those are partial, nonlinear, coupled differential equations and cannot be analytically solved at all times. On the other hand, they can be easily solved by finite differences methods, iterating for as long as it takes to reproduce the growth time of interest. The calculation gives then the profiles $\phi_i(u,\tau)$ of all species and the kinetics. Typical profiles at different growth times for a given value of c_{gas} are shown in Figure 1. The O_2 profiles are not straight lines as they are assumed to be in the steady-state regime [5]. Strictly speaking, steady-state is never attained as long as the oxide/Si interface moves deeper into the c-Si substrate. Furthermore, this interface is not sharp, in accordance with a wealth of experimental evidences [20,25,26]. Still in strict accordance with theoretical predictions [4,17,18] and experimental observations [19,20,25–27], a finite width region formed by Si in various lower oxidation states (+1, +2, +3, sub-oxides or Si-excess) early develops between the stoichiometric SiO_2 film and the c-Si substrate. In this way, O_2-Si reaction can take place in the whole region where non-fully oxidised Si is available.
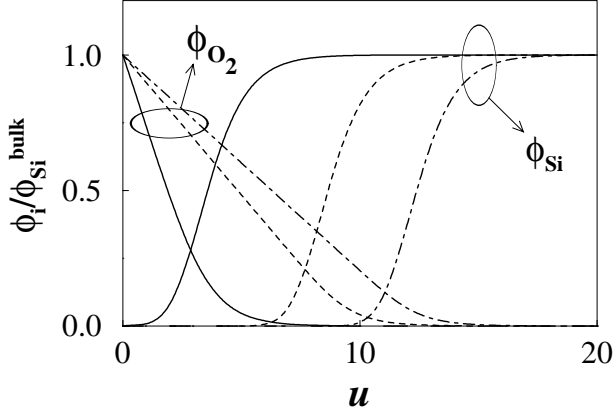
FIG. 1. Calculated Si and O_2 profiles in the solid phase at various temperatures and one pressure, for different oxidation times. The solid, dashed, and dot-dashed lines represent, respectively, the profiles at increasing oxidation times.

Fig. 1 shows that the two hypotheses of the Deal and Grove model are not valid: i) Steady-state regime is never attained; ii) reaction between O_2 and Si leading to growth does not take place at a sharp oxide/Si interface. For high enough temperatures and pressures, and long enough times, the O_2 profile approaches a straight line, and the thickness of the near-interface, sub-oxide region is much smaller than the oxide thickness. This is the observed situation at oxide thicknesses well above 20 nm. In this limit, steady state and abrupt interface are plausible approximations. In other words, asymptotically the Deal and Grove assumptions are valid, whereas at initial stages they are not. The kinetics in the initial growth regime, which was described as "anomalous" in the Deal and Grove framework, naturally emerges from the present model as follows. Let us consider the quantity that is mainly focused in practical situations: the oxide thickness χ. We calculate it through the relation:

$$\chi(\tau) = \int_0^\infty \phi_{oxide}(u,\tau)du = \int_0^\infty (1 - \phi_{Si}(u,\tau))du \quad (6)$$

The oxide growth kinetics $\chi(\tau)$ is completely determined by $\phi_{Si}(u,\tau)$, whose evolution is ruled by eqs.(5) and therefore is determined by a unique parameter c_{gas}, the concentration of O_2 in the gas phase. However, due to the particular form of the differential equations, together with boundary and initial conditions, the system presents a further scaling property. Suppose two different growth kinetics, with O_2 concentrations in the gas phase given by $c_{gas}^{(1)}$ and $c_{gas}^{(2)} = \alpha c_{gas}^{(1)}$, then the following relations apply

$$\phi_{O_2}^{(2)}(u,\tau) = \alpha \phi_{O_2}^{(1)}(u,\alpha\tau)$$
$$\phi_{Si}^{(2)}(u,\tau) = \phi_{Si}^{(1)}(u,\alpha\tau) \quad (7)$$
$$\chi^{(2)}(\tau) = \chi^{(1)}(\alpha\tau)$$

Therefore, besides collapsing for different temperatures

(i.e. different D and k) when natural units of the system are used, kinetic curves for different c_{gas} collapse to one single curve due to the symmetry present in the form of the diffusion-reaction model equations together with initial and boundary conditions. In summary, the theoretical prediction is that all kinetic curves reduce to a single one.

These predictions were tested with kinetic curves taken from references [6,27–29], corresponding to oxidations in Joule-effect heated and rapid thermal processing furnaces in a variety of growth parameters (temperature, O_2 pressure, and time) leading to oxide thicknesses ranging from 1 to 100 nm. In Fig. 2 we show the collapse of the experimental kinetics (symbols, colours) into the theoretical curve (line, black). For the kinetics curves from reference [28], with five points in each curve, we first used the scaling predicted by eqs.(7), obtaining four different curves, one for each temperature. We then scaled these curves using natural units for x and t according to eqs.(4) until they overlapped the theoretical curve. The curves from reference [6] contained much more experimental points, extending from 0.1 to 1000 min, and from 1 to 80 nm. For these curves the pressure scaling predicted by eqs.(7) is not perfect at long growth times, probably due to an increase in diffusivity. They were then collapsed one by one into the theoretical curve using eqs.(4) first, and then eqs.(7). The same procedure was used to collapse the kinetics from references [27,29] into the theoretical curve.
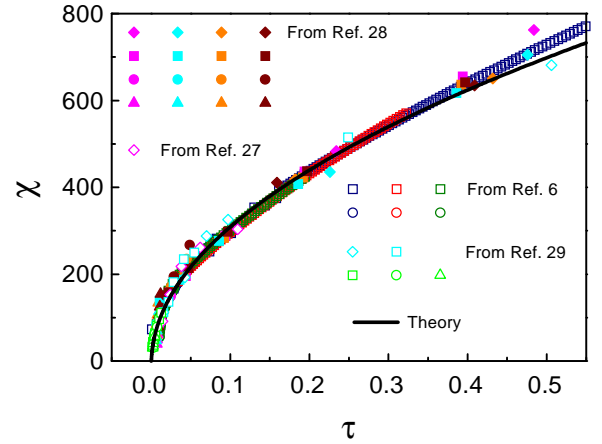

FIG. 2. Calculated growth kinetics (solid line, black) and experimental growth kinetics from the indicated references (symbols, colours) collapsed into the calculated curve.

The asymptotic depart from the theoretical curve is an expected result, since the present model assumes a constant diffusivity throughout the whole growth process, despite many evidences that this is not the case: i) transport of the diffusing species through the O-excess region near the surface [12,14,16,30], through the Si-excess region near the oxide/Si interface [15,18,25,26], and through the stoichiometric SiO_2 in the bulk of the

growing oxide film have different diffusivities; ii) the growth of the defective, near-surface and near-interface regions saturate within a few nm [12,19,20,27,30], while the bulk, stoichiometric oxide grows continuously. So, interstitial diffusion of O_2 through the bulk of the growing oxide gives a relative contribution that increases as the width of this region becomes dominant; iii) oxidations performed in dry O_2 flow during long time intervals (hours) may suffer from water vapor contamination, which accelerates the oxide growth [8,13].

Taking the dimensional oxide thickness $X(t) = \chi(\tau)\sqrt{\frac{D}{k}}$, and defining $\rho_O = \rho_{O_2}(0,t) = \frac{c_{gas}f_v}{c_{Si}^{bulk}}$, the asymptotic solution to eqs.(5) predicts the inverse growth rate $dt/dX = \frac{1.3}{D\rho_O}X$, with D constant, which is very similar to the asymptotic approximation of the Deal and Grove model [5] $dt/dX = \frac{1}{D\rho_O}X$. In Fig. 3 the inverse growth rate is plotted as a function of oxide film thickness for different experimental kinetics [6].
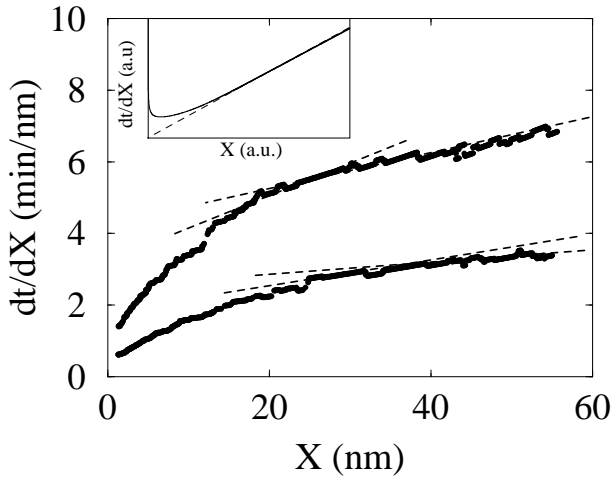

FIG. 3. Experimental inverse growth rates [6] and theoretical inverse growth rate (inset).

A deviation from a straight line in the thick film range is apparent, corresponding to a variable, increasing diffusivity, contrary to the theoretical prediction shown in the inset.

Thus, the thermal growth of silicon oxide films on c-Si in dry O_2 is promoted by diffusion of O_2 through the growing oxide with variable diffusivity. Similar physical arguments could support a variable diffusion rate. Nevertheless, even using constant, effective values for the diffusivity and reaction rate, modelling the growth as a diffusion-reaction process where conditions such as initial thickness, steady-state regime, and reaction solely at an abrupt interface are abandoned allows to reproduce the observed kinetics, especially in the lower thickness (ultra-thin film) regime which is the one of present and future practical interest. Realistic model evaluations of variable diffusivity and reaction rate stay beyond the scope of the present work, although this seems to be the only route

to a quantitative description of the complete growth kinetics.

The present approach opens the possibility of incorporating new and determinant facts on O_2 transport at initial stages of thermal oxide growth and on structure of the oxide/Si interface, that were discovered after the proposal of Deal and Grove [5] and not yet integrated into growth kinetics models. Some were discussed here, like the graded, Si-excess nature of the oxide/Si interface and the incorporation of freshly arriving O_2 into different regions of the growing oxide, while several others may also be included in a diffusion-reaction approach, such as the role played by oxygen excess centers [30] in the near-surface region on oxygen transport which has been recently investigated [16].

[1] Buchanan, D. A. and Lo, S. H. Growth, in *The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface-3* Vol 96-1 (eds. Massoud, H. Z., Poindexter, E.H., and Helms, C.R.) 3-14 (The Electrochemical Society, Pennington, 1996).

[2] Feldman, L.C., Gusev, E.P., and Garfunkel, E. in *Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices* (eds. Garfunkel, E., Gusev, E.P, and Vul', A.) 1-24 (Kluwer Academic Publishers, Dordrecht, 1998).

[3] Schuegraf, K. F. and Hu, C. Reliability of Thin SiO₂ *Semicond. Sci. Technol.* **9**, 989-1006 (1994).

[4] Pasquarello, A., Hybertsen, M.S., and Car, R. Interface structure between silicon and its oxide by first principles molecular dynamics *Nature* **396**, 58-60 (1998)

[5] Deal, B.E. and Grove, A. S. General Relationship for the Thermal Oxidation of Silicon *J. Appl. Phys.* **36**, 3770-3778 (1965).

[6] Massoud, H. Z., Plummer, J. D., and Irene, E. A. Thermal Oxidation in Dry Oxygen Growth-Rate Enhancement in the Thin Regime *J. Electrochem. Soc.* **132**, 2685-2693 (1985).

[7] Han, C. -J. and Helms, C.R. Parallel oxidation mechanism for Si oxidation in dry O₂ *J. Electrochem. Soc.* **134**, 1297-1302 (1987).

[8] Rigo, S. in *Instabilities in silicon devices* Vol. 1 (eds. G. Barbottin and A. Vapaille) 5-100 (Elsevier Publishers, Amsterdam, 1986) (1986).

[9] Plummer, J. D. in *The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface-3* Vol 96-1 (eds. Massoud, H. Z., Poindexter, E.H., and Helms, C.R.) 129-142 (The Electrochemical Society, Pennington, 1996).

[10] Deal, B.E. in *The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface*, (eds. Helms, C. R. and Deal, B.E.) 5-16 (Plenum Press, New York, 1988).

[11] Han, C.-J. and Helms, C.R. ¹⁸O Tracer Study of Si Oxidation in Dry O₂ Using SIMS *J. Electrochem. Soc.* **35**, 1824-1832 (1988).

[12] Trimaille, I., Stedile, F.C., Ganem, J.-J., Baumvol,

I.J.R., and Rigo, S. in *The Physics and Chemistry of SiO$_2$ and the Si-SiO$_2$ Interface-3* Vol 96-1 (eds. Massoud, H. Z., Poindexter, E.H., and Helms, C.R.) 59-71 (The Electrochemical Society, Pennington, 1996). Pennington (1996).

[13] Rochet, F., Rigo, S., Froment, M., D'Anterroches, C., Maillot, C., Roulet, H., and Dufour, G. The thermal oxidation of silicon. The special case of the growth of very thin films *Adv. Phys.* **35**, 237-274 (1986).

[14] Trimaille I. and Rigo, S. Use of ^{18}O isotopic labeling to study the thermal dry oxidation of silicon as a function of temperature and pressure *Appl. Surf. Sci.* **39**, 65-80 (1989).

[15] Lu, H.C., T. Gustafsson, T., Gusev, E.P., and Garfunkel, E. An isotopic labeling study of the growth of thin oxide films on Si(100) *Appl. Phys. Lett.* **67**, 1742-1744 (1995).

[16] Hamann, D.R. Diffusion of Atomic Oxygen in SiO$_2$ *Phys. Rev. Lett.* **81**, 3447-3450 (1998).

[17] Mott, N.F., Rigo, S., Rochet, F., and Stoneham, A.M. Oxidation of Silicon *Phil. Mag.* **B60**, 189-212 (1988).

[18] Stoneham, A.M., Grovenor, C.R.M., and Cerezo, A. Oxidation and the structure of the silicon oxide interface *Phil. Mag.* **B55**, 201-210 (1986).

[19] Himpsel, F.J., McFeely, F.R., Taleb-Ibrahimi, A., Yarmoff, J.A. and Hollinger, G. Microscopic structure of the SiO$_2$/Si interface *Phys. Rev.* **B38**, 6084-6096 (1988).

[20] Jackman, T.E., MacDonald, J.R., Feldman, L.C., Silverman, P.J. and Stensgaard, I., (100) and (110) Si-SiO$_2$ interface studies by MeV ion backscattering *Surf. Sci.* **100**, 35-42 (1980).

[21] Mattis, D.C. and Glasser, M.L. The uses of quantum field theory in diffusion-limited reactions *Rev. Mod. Phys.* **70**, 979-1001 (1998).

[22] Larralde, H., Araujo, M., Havlin, S., and Stanley, H.E. Diffusion reaction kinetics for A + B(static) → C(inert) for one-dimensional systems with initially separated reactants *Phys. Rev.* **A46**, R6121-R6123 (1992)

[23] Barkema, G.T., Howard, M.J., and Cardy, J.L. Reaction-diffusion front for A + B → 0 in one dimension *Phys. Rev.* **E53**, R2017-R2020 (1996).

[24] Pretorius, R., Strydom, W., Mayer, J.W., and Comrie C. ^{31}Si tracer studies of the oxidation of Si, CoSi and PtSi *Phys. Rev.* **B22**, 1885-1891 (1980). See also Baumvol, I.J.R., Krug, C., Stedile, F.C., Gorris, F., and Schulte, W.H. On the immobility of Si during thermal growth of ultrathin silicon oxide films on Si(111) in O$_2$, submitted for publication in Phys. Rev. Lett., January, 1999.

[25] Gusev, E.P., Lu, H.C., Gustafsson, T., and Garfunkel, E. Growth mechanisms of thin silicon oxide films on Si(100) studied by medium-energy ion scattering *Phys. Rev.* **B52**, 1759 -1775 (1995).

[26] Gusev, E.P., Lu, H.C., Gustafsson, T., and Garfunkel, E. The initial oxidation of silicon: new ion scattering results in the ultra-thin regime *Appl.Surf. Sci.* **104/105**, 329-334 (1996).

[27] Stedile, F.C., Baumvol, I.J.R., Oppenheim, I.F., Trimaille, I., Ganem, J.-J., and Rigo, S. Thickness of the SiO$_2$/Si interface and composition of silicon oxide thin films: effect of wafer cleaning procedures *Nucl. Instrum. Meth.* **B118**, 493-498 (1996).

[28] Kamigaki, Y. and Itoh, Y. Thermal oxidation of silicon in various oxygen partial pressures *J. Appl. Phys.* **48**, 2891-2896 (1977).

[29] Ganem, J.-J., Rigo, S., and Trimaille, I. Modellization of the silicon rapid thermal oxidation in the initial stages according to the silicon fragments model *Microelec. Eng.* **22** 35-38 (1993).

[30] Stesman, A. and Scheerlink, F. Generation aspects of the delocalized intrinsic EX defect in thermal SiO$_2$ *J. Appl. Phys.* **75**, 1047-1058 (1994).

ACKNOWLEDGEMENTS